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we find that CdSe is blocking to the oxidation of the reduced form of the redox couple in the dark, but illumination results in its oxidation. The photoanodic current peak in a cyclic voltammogram occurs more negative than at a Pt electrode, the difference between these values is the photovoltage, E_y , taken to approximate the barrier height, E_g . For E° between -1.2 and -0.1 V vs. SCE, E_y increases as E° increases in a nearly ideal manner. Thus, E_g increases nearly linearly as E° moves positive of the flat-band potential, E_{fb} , of -1.2 V vs. SCE. For E° more positive than -0.1 V vs. SCE E_y is constant, independent of E° . The effect of a number of different etches on the interface energetics of CdSe was investigated, since it was previously determined that an oxidizing or reducing etch would yield quite different results for n-CdTe. For CdSe, however, the different etches do not give significantly different results with respect to E_g vs. E° , despite large variation in surface composition deduced from Auger and XPS spectra. The highest E_y obtained is -0.8 V using $\text{Fe}(\text{C}_5\text{Me}_5)_2^{+0}$ and more positive redox couples. In general, with respect to E_g vs. E° , n-type CdSe more closely mimics the behavior of CdS than CdTe, despite the fact that the band gap of CdSe ($E_g = 1.7$ eV) is closer to that of CdTe ($E_g = 1.4$ eV) than to CdS ($E_g = 2.4$ eV).

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"CHARACTERIZATION OF THE INTERFACE ENERGETICS FOR N-TYPE

CADMIUM SELENIDE/NON-AQUEOUS ELECTROLYTE JUNCTIONS"

by

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Characterization of the Interface Energetics for N-Type
Cadmium Selenide/Non-Aqueous Electrolyte Junctions

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Abstract

→ Single-crystal, n-type CdSe photoanodes have been studied in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4/\text{CH}_3\text{CN}$ solutions containing low concentrations of fast, outer-sphere, one electron redox reagents. A number of redox couples were studied spanning a wide range of redox potentials, E° . We find that reversible electrochemical response is seen at both dark and illuminated (632.8 nm light) n-CdSe for couples with E° more negative than -1.2 V vs. SCE, e.g. $\text{Ru}(\text{bpy})_3^{2+/+}/\text{O}/\text{H}^+$. For couples with E° positive of -1.2 V vs. SCE we find that CdSe is blocking to the oxidation of the reduced form of the redox couple in the dark, but illumination results in its oxidation. The photoanodic current peak in a cyclic voltammogram occurs more negative than at a Pt electrode, the difference between these values is the photovoltage, E_y , taken to approximate the barrier height, E_b . For E° between -1.2 and -0.1 V vs. SCE, E_y increases as E° increases in a nearly ideal manner. Thus, E_b increases nearly linearly as E° moves positive of the flat-band potential, E_{fb} , of -1.2 V vs. SCE. For E° more positive than -0.1 V vs. SCE E_y is constant, independent of E° . The effect of a number of different etches on the interface energetics of CdSe was investigated, since it was previously determined that an oxidizing or reducing etch would yield quite different results for n-CdTe. For CdSe, however, the different etches do not give significantly different results with respect to E_b vs. E° , despite large variation in surface composition deduced from Auger and XPS spectra. The highest E_y obtained is ~0.8 V using $\text{Fe}(\text{C}_5\text{Me}_5)_2^{+/0}$ and more positive redox couples. In general, with respect to E_b vs. E° , n-type CdSe more closely mimics the behavior of CdS than CdTe, despite the fact that the band gap of CdSe ($E_g = 1.7$ eV) is closer to that of CdTe ($E_g = 1.4$ eV) than to CdS ($E_g = 2.4$ eV).

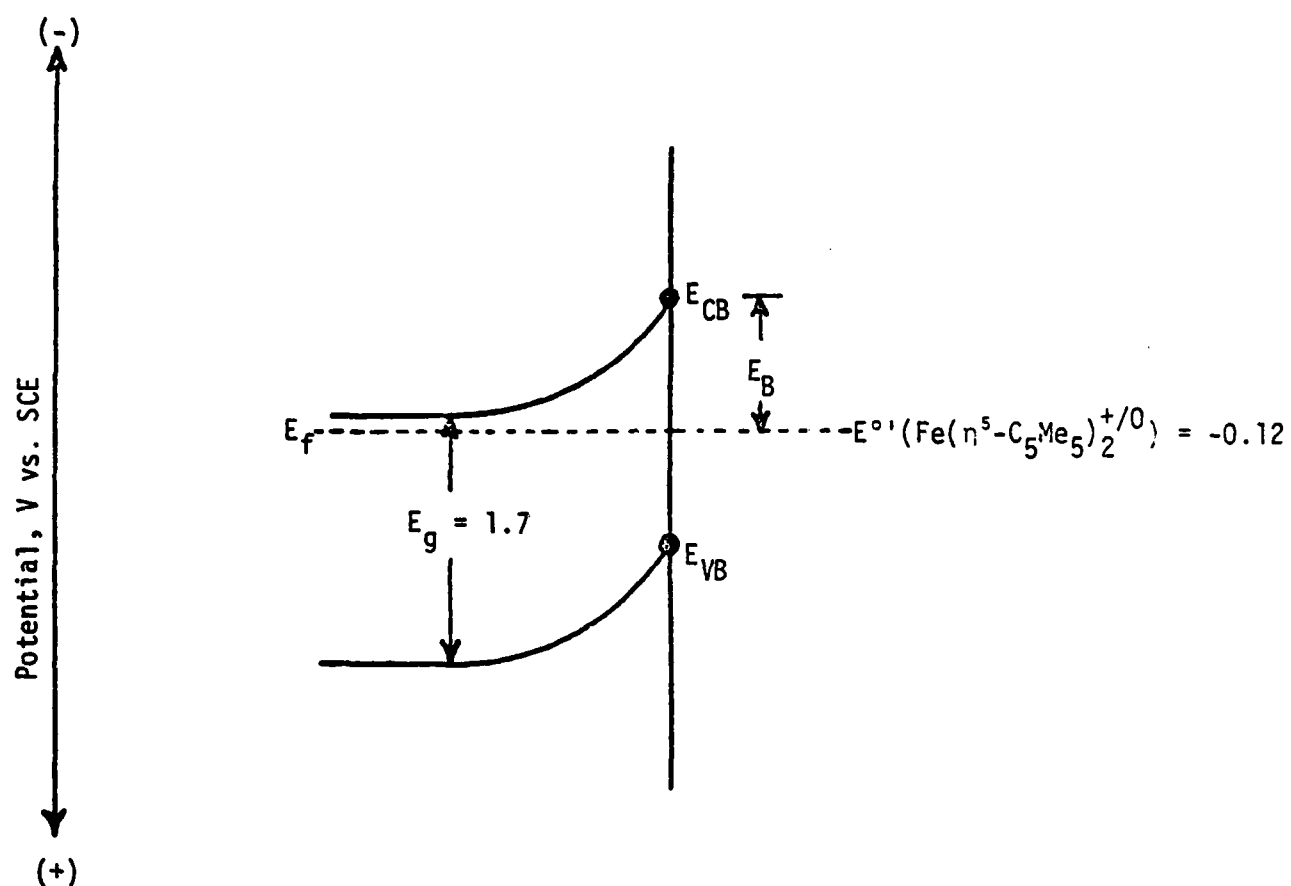
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Results from this laboratory have been reported for the interface energetics of n-type CdS ($E_g = 2.4$ eV) and CdTe ($E_g = 1.4$ eV) photoanodes.^{1,2} CdS was found to nearly fit the ideal model^{1,3,4} of a semiconductor/liquid electrolyte interface that follows from the considerations for an ideal semiconductor/metal interface.⁴ Reversible electrochemical response was obtained in the dark for couples with redox potentials, $E^{\circ'}$, more negative than the conduction band edge, E_{CB} , Scheme 1. For couples with $E^{\circ'}$ positive of E_{CB} and negative of the onset of decomposition current the open-circuit photovoltage, E_V , was found to vary linearly with $E^{\circ'}$ as predicted by equation (1), where E_{FB} is the electrochemical potential of the semiconductor, E_f , when

$$E_V = E_B = |E^{\circ'} - E_{FB}| \quad (1)$$

there is no band bending, and E_B is the barrier height, $|E_{CB} - E^{\circ'}|$. The ideal model leads to the expectation that only couples having $E^{\circ'}$ more positive than the conduction band edge, E_{CB} , would have output photovoltage. Couples near the top of the valence band, E_{VB} , would have the highest photovoltage. In the ideal model we assume that E_{VB} and E_{CB} remain fixed relative to a reference for $E^{\circ'}$ no more than E_g positive of E_{CB} , and thus changes in $E^{\circ'}$ will result in changes in E_V .¹⁻⁴

With respect to E_B vs. $E^{\circ'}$, CdTe was found to behave quite differently depending on whether it was etched with an etch containing oxidizing or reducing agents.² For CdTe etched with an oxidizing etch non-ideal behavior is obtained. The open-circuit photovoltage does not obey equation (1), but instead E_V is constant at ~ 0.5 V regardless of the $E^{\circ'}$ of the couple used. Couples with $E^{\circ'}$ from -2.0 to $+0.7$ V vs. SCE were studied spanning a potential range larger than the separation of E_{CB} and E_{VB} . N-type CdTe was concluded to be Fermi level



Scheme I Representation of the interface energetics for n-CdSe in contact with a redox couple in an electrolyte solution.

pinned.⁵ This refers to a situation in which a semiconductor is measured to have a constant barrier height, E_B , independent of the contacting medium over a wide range of redox potentials. This is analogous to the behavior obtained for some semiconductor/metal (Schottky barrier) interfaces, where the work function of the metal should determine the barrier height for an ideal semiconductor.^{4,6} But for a number of semiconductor/metal interfaces E_B is essentially independent of the work function of the metal over a wide range of work functions.⁶ This is referred to as Fermi level pinning for a semiconductor/metal interface, and is analogous to an E° independent E_B for a semiconductor/electrolyte interface. In the ideal model the band edges, E_{CB} and E_{VB} , remain fixed relative to a reference as redox couple potential is varied, whereas with Fermi level pinning E_B is fixed, the band edges move and the potential changes occur across the Helmholtz layer, not across the semiconductor. When carrier inversion occurs the E_V can be independent of E° ,^{7,8} but inversion occurs only when the band bending is $>1/2 E_g$ at charge transfer equilibrium. For CdTe^2 the band bending is 0.5 V, and for TiO_2^9 and SrTiO_3^9 the band bending is also $<1/2 E_g$. In such cases the E° independent E_V is attributable to surface states.^{5,9}

Interestingly, for CdTe etched with a reducing etch the behavior obtained is nearly ideal.² Thus, the reducing etch presumably removes oxidized material which causes Fermi level pinning. The emphasis of this study has been to measure the effects of different etches on the electrochemical behavior of CdSe , in particular to determine whether Fermi level pinning occurs and whether it can be induced or removed with an oxidizing or reducing etch. For CdSe $E_g = 1.7 \text{ eV}$ placing it between CdTe and CdS in terms of E_g . In addition the nature of the oxidized material formed on the surface of each of these three semiconductors

when etched with an oxidizing etch is quite different. S is an insulator, Se a semiconductor, and Te is a very small band gap semiconductor. Thus, whether Fermi level pinning occurs may depend on the material formed on the surface by an oxidizing etch, and the distribution, density, and nature of surface states associated with it. These properties should be quite different for S, Se (or SeO_x , Se_x^{2-}), and Te (or TeO_x , Te_x^{2-}), and we do find rather different behavior from CdS, CdSe, and CdTe photoanodes.

The solid state data for CdX/metal (Schottky barrier) interfaces show different behavior for $X = \text{S}, \text{Se}, \text{and Te}$. For CdS E_g is shown to vary from 0 to 0.85 V as the work function of the metal varies, while for CdTe E_g is almost constant varying from ~ 0.6 V to ~ 0.8 V for a range of work functions spanning ~ 2 V.^{6,10} For CdSe E_g also appears constant for the metals used, however, the range of work functions for the metals used was not as large as for CdS/metal or CdTe/metal interfaces.⁶ Thus, it is possible that E_g might decrease and drop to zero for metals with smaller work functions. We now report our results for CdSe/liquid electrolyte interfaces that show behavior with respect to E_g vs. E° that is very similar to CdS, despite the significantly smaller band gap of CdSe.

Experimental

Electrode Fabrication. Oriented single crystals of n-CdSe, (001) plane exposed, $\sim 0.9 \Omega\text{-cm}$, were obtained from Cleveland Crystals, Inc., Cleveland, Ohio. The crystals were polished first with $20 \mu\text{m}$ alumina and then with $10 \mu\text{m}$ alumina on a polishing glass. The crystals were finished with $0.3 \mu\text{m}$ alumina on a polishing cloth (Politex Supreme PS, Gros Corp., Stamford, CT), fixed onto the glass. Ohmic contact was made to the CdSe by rubbing Ga-In eutectic onto the back of the crystal. A Cu wire was attached using Ag epoxy. The Cu wire was encased in a 4 mm Pyrex tube and all surfaces but the exposed front surface of CdSe were sealed with ordinary epoxy. The exposed surface of the CdSe (typically $3 \times 3 \text{ mm}$ in dimensions) was the (001) face. Just prior to use all electrodes were etched and cleaned as described below.

CdSe Etching Procedures. The CdSe pretreating etch was one of the following: (i) 5% Br_2/MeOH for 30 s at 25°C followed by rinsing with MeOH, (ii) 4g $\text{K}_2\text{Cr}_2\text{O}_7$, 10 ml conc. HNO_3 , and 20 ml H_2O for 30 s at 25°C followed by rinsing with distilled H_2O , (iii) an acid etch consisting of conc. $\text{HNO}_3/\text{conc. H}_2\text{SO}_4/\text{glacial acetic acid}/\text{conc. HCl}$ (30/20/10/0.1 by volume) for 8 s at the mixing temperature followed by a rinse with conc. H_2SO_4 for 15 s at 25°C followed by rinsing with distilled H_2O , or (iv) the reducing pretreatment which involved first the oxidizing etch (i) or (ii) followed by immersion into a boiling solution of 2.5 M NaOH and $0.6 \text{ M Na}_2\text{SO}_4$ for 3 min. The electrode was then liberally rinsed with distilled H_2O .

Chemicals. Spectrograde CH_3CN was freshly distilled from P_2O_5 prior to use. The $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ from Southwestern Analytical Chemicals was vacuum dried at 70°C for 24 h prior to use, and NaClO_4 was obtained from commercial sources

and used without further purification. Triply distilled H₂O was used for solvent in aqueous electrolyte systems. All chemicals used for etching were reagent grade except for Na₂S₂O₄ which was purified (low in iron).

Redox reagents were generally obtained from commercial sources; TMPD was purified by sublimation; Fe(ⁿ5-C₅H₅)₂ was used as received. Other redox couples are those used and purified in this laboratory previously.^{1,2} Abbreviations for redox couples are MV²⁺ \equiv N,N'-dimethyl-4,4-bipyridinium and TMPD \equiv N,N,N',N'-tetramethyl-p-phenylenediamine. The E°' values are from cyclic voltammograms at Pt or Hg electrodes. The E°' value was taken to be the average position of the anodic and cathodic peaks in the cyclic voltammogram.

Electrochemical Equipment and General Procedures. Electrolyte solutions were CH₃CN/0.1 M [n-Bu₄N]ClO₄. The non-aqueous electrolyte solution was passed through anhydrous, neutral Al₂O₃ just prior to use to insure dryness. All electrochemistry was carried out under a positive pressure of pure Ar.

Cyclic voltammograms were obtained using a PAR model 173 potentiostat driven by a PAR model 175 programmer. Data were recorded on a Houston Instruments X-Y recorder. The electrochemical cell was a single-compartment cell consisting of a working electrode of n-CdSe, Pt, or Hg, a Pt counter-electrode, and a reference electrode. A 0.1 M AgNO₃/Ag/0.1 M [n-Bu₄N]ClO₄/CH₃CN reference (+0.35 V vs. SCE) was used as the reference electrode. All E_g determinations are from cyclic voltammograms at 100 mV/s.

For cyclic voltammograms redox reagents were added to solution at ~1 mM concentration in all cases. The photoelectrodes were illuminated using a beam expanded He-Ne laser from Coherent Radiation, providing ~50 mW/cm² at 632.8 nm. This is sufficient light intensity to insure that photocurrent for ~1 mM solutions of redox reagent is limited by diffusion, not excitation rate (light intensity).

XPS and Auger Studies. Auger spectra were obtained on a Physical Electronics Model 590A scanning Auger spectrophotometer. A 5 KeV electron beam with a beam current of 0.1 to 1 μ A was used as the excitation source. The samples were mounted by attaching the Cu wire lead to the sample holder to insure electrical grounding. A Physical Electronics Model 04-303 differential ion gun was used to produce a 2 KeV Ar^+ ion beam for sputtering. The pressure was maintained at $\sim 3 \times 10^{-8}$ torr in the main vacuum chamber and 1.5×10^{-4} torr of Ar in the ionization chamber, while sputtering.

X-ray photoelectron spectra (XPS) were obtained on a Physical Electronics Model 548 spectrometer with a magnesium anode. The broad scans (0-1000 eV) were recorded with a pass energy of 100 eV and the narrow scans with a pass energy of 25 eV. The peak energies of the Cd and Te peaks were referenced to the C 1s binding energy (284.6 eV) to correct for charging. Samples were mounted as above and sputtering was done with a 5 KeV Ar^+ beam, after introducing Ar into the vacuum chamber to bring the pressure to $\sim 7 \times 10^{-5}$ torr. Elements detected by Auger and XPS were identified by reference to data previously reported using these techniques.^{11,12}

Results

The barrier height, E_B , is taken to be equal to the maximum photovoltage, E_V , obtained from the n-CdSe anode. At least, E_V gives a good, reproducible value, though E_V underestimates E_B by at least 0.1 V owing to the difference in E_{CB} and E_{FB} , cf. Scheme I. Cyclic voltammetry of various redox couples at Pt and dark and illuminated n-CdSe has been examined in quiet solutions of $CH_3CN/0.1\text{ M } [n\text{-Bu}_4N]ClO_4$ to measure E_V . Low concentration of redox reagents were used ($\sim 1\text{ mM}$), to make sure that currents observed are not limited by light intensity, and redox couples having fast kinetics were used to insure that the data reflect properties associated with variation in E° and the semiconductor energetics. Further, the choice of redox couples has been restricted to fast one-electron, outer-sphere reagents to minimize complications from adsorption such as I^- on $MoSe_2$ ¹³ and S^{2-} on CdS .¹⁴ The photovoltage, $E_V \approx E_B$, is obtained by comparing the position of the peak of photoanodic current for a given redox couple at n-CdSe, $E_{PA,CdSe}$, with the peak of anodic current, $E_{PA,Pt}$ at a reversible Pt electrode, equation (2).

$$E_B \approx E_V = |E_{PA,CdSe} - E_{PA,Pt}| \quad (2)$$

The anodic current peak is the approximate potential at which there is a 1/1 ratio of the oxidized and reduced form of the redox couple near the surface of the electrode. Thus, E_V is the extent to which the anodic peak on illuminated n-CdSe is more negative than at a Pt electrode. With high enough light intensity this is the maximum photovoltage. Equation (2) then gives E_B to within 100 mV. There are five classes for electrochemical behavior of fast, one-electron, redox couples at n-type semiconductor electrodes.¹⁵ These are as follows:

Class I - $E^{\circ'}$ is sufficiently negative that reversible behavior is observed at the semiconductor; $E^{\circ'}$ is more negative than E_{CB} and there is no photoeffect.

Class II - $E^{\circ'}$ is near E_{CB} but slightly positive of it so that dark oxidation is observed but rate is poor and is improved by irradiation with a small negative shift of the anodic current peak.

Class III - There is no dark oxidation of the reduced form of the couple; E_g depends on $E^{\circ'}$ such that E_g is proportional to $|E^{\circ'} - E_{FB}|$ for $E^{\circ'}$ between E_{FB} and E_{VB} .

Class IV - There is no dark oxidation of the reduced form of the couple but E_g is independent of $E^{\circ'}$.

Class V - Redox couples have $E^{\circ'}$ sufficiently negative or positive that the decomposition current for the electrode is too great to allow study of the redox couple.

We have used this classification scheme in this characterization of the behavior of CdSe electrodes in CH_3CN solutions. A number of etches have been used to pretreat and/or clean the surface. Among these are oxidizing etches ($K_2Cr_2O_7/HNO_3$, Br_2/CH_3OH) and a reducing etch ($Na_2S_2O_4/NaOH$). We found previously with CdTe that these oxidizing and reducing etches give the different results mentioned above.²

Table I summarizes the data for determination of E_g for n-CdSe. Variation in E_g for independently prepared samples is <100 mV for a given redox couple. Table I and Figure 1 show that the $Ru(bpy)_3^{2+/+0/-}$ couples all give reversible behavior in the light or in the dark at n-CdSe. Thus, according to the ideal model, E_{FB} must be more positive than -1.3 V vs. SCE. Since some photovoltage is observed for the $MV^{+}/0$ couple (~ 260 mV) E_{FB} is placed at ~ -1.2 V. A larger photovoltage is observed for $MV^{2+}/+$ (~ 350 mV),

however, two, one-electron photoanodic peaks are still discernible corresponding to $MV^0 \rightarrow MV^+$ and $MV^+ \rightarrow MV^{2+}$. For a completely ideal case only one, two-electron wave would be observed, since both $E^\circ(MV^{2+}/+)$ and $E^\circ(MV^+/0)$ are positive of E_{FB} . Thus, when MV^0 can be oxidized MV^+ should also be able to be oxidized. The separation of the two photoanodic waves is less than at Pt, and the fact that two waves are discernible is probably associated with interface states which facilitate back electron transfer.^{5,15} In the dark no current at all is seen for the $MV^{2+}/+$ couple as expected for a couple positive of E_{FB} . Figure 2 shows cyclic voltammograms for $Fe(n^5-C_5Me_5)_2^{2+/0}$ at Pt and illuminated n-CdSe showing an $E_g = -0.8$ V. Scheme I represents the interface energetics in this case. The waves for $Fe(n^5-C_5Me_5)_2^{2+/0}$ are somewhat broader on CdSe than on Pt. However, the peak current is still proportional to $(\text{scan rate})^{1/2}$, as expected for a diffusion limited oxidation process. The data for couples with more positive E° ($TMPD^{2+}/+ / 0$ and $Fe(C_5Me_5)_2^{2+/0}$) seem to indicate that the photo-voltage reaches ~ 800 mV for $E^\circ \approx -0.2$ V vs. SCE then levels off and is independent of E° . This is indicative of Class IV behavior positive of -0.20 V vs. SCE and could mean that the maximum ideal photovoltage is not obtained due to photoanodic decomposition processes. Photoanodic corrosion of CdSe is known to occur, equation (3).¹⁶ The data from Figures 1 and 2 and Table I were



taken on the first several scans after etching the electrode in Br_2/CH_3OH , since some surface changes occur after repeated scanning. Couples having E° more positive than $+0.7$ V vs. SCE cannot be examined, owing to severe photoanodic corrosion of the n-CdSe. Thus, couples with E° more positive than $+0.7$ V vs. SCE are assigned to Class V in $CH_3CN/0.1$ M $[n-Bu_4N]ClO_4$. Indeed, it appears that E_g declines somewhat for the more positive redox couples and we

attribute this to decomposition of the surface to yield a film of Se on the surface. Generally, couples negative of -0.0 V vs. SCE will give a constant E_g for many scans when the electrode potential is not taken more than 100 mV more positive than the photoanodic peak. For the more positive couples photoanodic corrosion leads to lower photovoltage even after <5 scans.

Etches other than $\text{Br}_2/\text{CH}_3\text{OH}$ have been used to pretreat the electrode surface, but the best cyclic voltammograms, in terms of peak width and separation of the anodic and cathodic peaks, were obtained using a $\text{Br}_2/\text{CH}_3\text{OH}$ etch. Other etches used are listed in the Experimental, and include both oxidizing ($\text{K}_2\text{Cr}_2\text{O}_7/\text{HNO}_3$) and reducing etches ($\text{Na}_2\text{S}_2\text{O}_4/\text{NaOH}$). Auger spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used to examine etched n-CdSe electrodes and to determine whether differences in the quality of electrochemical behavior using different etches could be correlated to surface stoichiometry. Auger and XPS spectra of oxidized, reduced, and sputtered n-CdSe surfaces do reveal large differences in the ratio of Cd/Se as shown in Figure 3. Using either $\text{Br}_2/\text{CH}_3\text{OH}$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{HNO}_3$ as the oxidizing etch gives similar spectra to the ones shown in the middle. Table II gives the Cd/Se signal ratios obtained by Auger spectroscopy for n-CdSe electrodes etched with a variety of etchants. There is considerable variation in the values obtained using a given etch, thus the values given are only approximate. However, it can be easily seen that the ratio of Cd/Se is significantly lower for electrodes etched using an oxidizing etch than for electrodes etched with a reducing etch or Ar^+ sputter. The HCl etch gives a similar ratio to that for a sample etched with a reducing etch. The ratios obtained are essentially independent of whether the Cd or Se face was exposed, when any etch was used except the HCl etch. Using the HCl etch the average

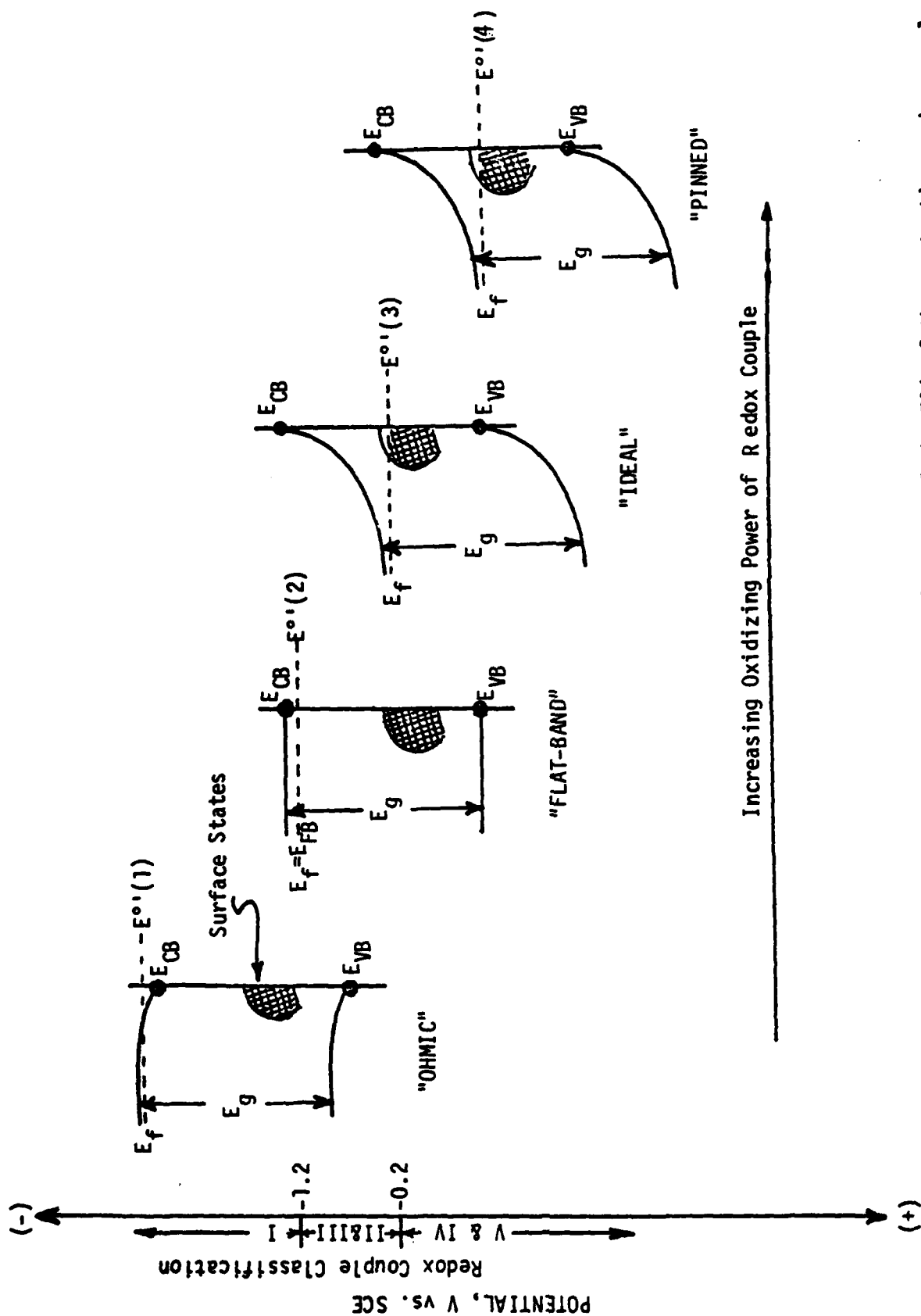
value obtained for the Cd/Se ratio was somewhat higher (~40%) for the Se face than for the Cd face. The range of values obtained for each face was fairly large, and the ranges of values for the two faces do overlap each other. This result may be due to differences in topography of the two surfaces. The HCl etch produces a smooth mirrored finish on the Cd face and a dull surface consisting of microscopic 6-sided pyramids on the Se face. Since the escape depth (and thus sampling depth) for the Cd (376 eV) and Se (1315 eV) electrons are significantly different,¹⁷ changes in topography could change the ratio of Cd/Se detected. All other etches produced smooth finishes.

In spite of the large differences in Cd/Se ratios obtained for different etches there appears to be no correlation between the electrochemical data and the surface analytical results. Poor electrochemical behavior is obtained using etches that produce low as well as high Cd/Se ratios. It is evident from the Auger data that the oxidizing etches leave a surface rich in Se. However, this does not cause Fermi level pinning over the entire potential found for n-CdTe etched with an oxidizing etch.²

Discussion

Despite rather large surface composition changes from different etches, Table II, the behavior of n-CdSe with respect to E_B vs. E° of a contacting redox couple is independent of the etch. In particular, Class I behavior is exhibited by $\text{Ru}(\text{bpy})_3^{2+/1+/0/1-}$ at all n-CdSe surfaces. This result stands in contrast to that for n-CdTe for the same solvent/electrolyte/redox couple where an oxidizing etch gives Class IV behavior and a reducing etch gives Class I behavior.² In fact, the behavior of n-CdSe closely resembles that for n-CdS¹ in that there is an ~1.0 V range of E° 's where E_B vs. E° is nearly ideal, Table III. For n-CdSe, though, the region more positive than -0.2 V vs. SCE gives no greater E_B out to the most positive E° . In the same region, n-CdS is likewise clearly non-ideal, but experimental data showing E_B to be completely independent of E° are not available owing to photoanodic corrosion for the very positive E° 's. As noted above, it is possible for photoanodic decomposition to account for a lowering of photovoltage, and E_B values for the most positive redox couple are likely lower for this reason. But for both n-CdS and n-CdSe the $\text{Ru}(\text{bpy})_3^{2+/1+/0/1-}$ couples are Class I, independent of surface pretreatment.

Further, both n-CdS and n-CdSe give an E_B vs. E° that is nearly ideal (Class II, III behavior) until some positive E° beyond which Class IV behavior is found. For n-CdSe the E_y associated with Class IV behavior is ~0.8 V, showing that the surface is not strongly inverted where E_B is independent of E° . Similarly, the E_y associated with Class IV behavior at n-CdS is ~0.9 V, less than $1/2 E_g$. The behavior of n-CdS and n-CdSe appears to be similar to that for n-TiO₂⁹ and n-SrTiO₃⁹ where there is a region below E_{cg} that is essentially free of surface states. But below E_{cg} the surface state density becomes sufficiently great that for some sufficiently positive



Scheme II

Interface energetics for n-CdSe as a function of the $E^{\circ'}$ of the contacting redox couple. For $E^{\circ'}$ more negative than $E_{FB} = -1.2V$ vs. SCE the redox couple makes an "ohmic" contact whereas couples between E_{FB} and $-0.2V$ vs. SCE nearly "ideal" variation in E_g obtains. For $E^{\circ'}$ more positive than $-0.2V$ vs. SCE the density of surface states is sufficiently high that additional potential drop across the interface occurs in the Helmholtz layer and not in the space charge layer of the n-CdSe and E_g is effectively fixed. Redox couples beyond $+0.7V$ vs. SCE give corrosion.

E°' (~ 0.2 V vs. SCE for n-CdSe) some potential drop occurs across the semiconductor, E_B , and any additional drop occurs across the Helmholtz layer, as shown in Scheme II for CdSe. It is noteworthy that CdSe gives an E_B about as large as for CdS, despite its 0.7 eV smaller E_g . The ratio E_B/E_g is even larger for reduced n-CdTe.²

At the oxidized surface of n-CdTe all redox couples exhibit Class IV behavior with $E_B \sim 0.5$ V.² This is consistent with an overlayer of material on the n-CdTe that behaves as a metal with a work function that gives an E_B of 0.6 V.⁵ For such a situation the E_y measured by cyclic voltammetry would be independent of E°' , since the electrode would behave as a buried Schottky barrier. We proposed that the oxidized overlayer is a Te-rich layer, removable by reduction with $S_2O_4^{2-}$.² While a Te overlayer could serve as a metal to form a Schottky barrier on CdTe, the oxidation of CdSe does not lead to a surface layer having such properties.

The use of cyclic voltammetry to measure the interface energetics of semiconductor/liquid electrolyte interfaces is a technique that could lead to significant errors. Such a problem has been suggested in a recent study of p-GaAs.¹⁸ In the present case there appears to be good internal consistency, and the E_{FB} for CdSe determined here in CH_3CN is similar to that in H_2O in the absence of specifically adsorbed species such as S^{2-} .¹⁴ Further, while there may be an error of ~ 100 mV, the value of E_{FB} is rather well-defined by the fact that it is located between $E^\circ'(Ru(bpy)_3^{2+}/+)$ and $E^\circ'(MV^+/0)$ because the Ru system exhibits Class I behavior and the $MV^+/0$ is in Class III.

Data for metal/CdSe Schottky barrier systems are sparse,⁶ but the E_B determinations seem to give small E_B values compared to those from the liquid junction systems, Table III. The E_B data from the liquid junctions suggest that better Schottky barriers could possibly be made with CdSe by exploring a

wider range of barrier formation conditions. However, it should be emphasized that any metal/semiconductor contact will result in greater interface chemistry than is associated with the interaction with an outer-sphere redox couple such as $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2^{+/0}$. The metal/semiconductor interface energetics will likely vary in ways that depend on the chemistry that occurs as well as on variations in work function.¹⁹ The analogous complication in electrochemistry is the finding that different redox couples, having the same E° 's but differing chemistry give different E_B 's at a given semiconductor/solvent/electrolyte interface. For example, in the same aqueous electrolyte where E_{redox} of $\text{Fe}(\text{CN})_6^{3-/4-}$ and I_3^-/I^- can be the same, a different E_y would be obtained for n-MoS₂ and related metal dichalcogenides for these two couples.¹⁵ The I_3^-/I^- system gives a significantly larger E_y owing to its strong adsorption to the surface.¹⁵ Manipulating and exploiting metal/semiconductor or liquid/semiconductor interfaces depends on controlling the interface chemistry.

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Table I. Cyclic Voltammetry Data for Various Redox Couples at Pt and Illuminated n-Type CdSe

Couple	E° ^a	E _{pa} at PT ^b	E _{pa} at n-CdSe ^c	Class ^d
TMPD ²⁺ /1 ⁺	+0.72	+0.72	+0.12	IV
(biferrocene) ²⁺ /1 ⁺	+0.5	+0.52	-0.24	IV
Fe(η^5 -C ₅ H ₅) ₂ ¹⁺ /0	+0.43	+0.43	-0.34	IV
(biferrocene) ¹⁺ /0	+0.28	+0.31	-0.57	IV
TMPD ¹⁺ /0	+0.10	+0.14	-0.42	IV
Fe(η^5 -C ₅ Me ₅) ₂ ¹⁺ /0	-0.12	-0.07	-0.87	III
MY ²⁺ /1 ⁺	-0.45	-0.41	-0.76	III
MY ¹⁺ /0	-0.85	-0.82	-1.08	III
Ru(bpy) ₃ ²⁺ /1 ⁺	-1.3	-1.26	-1.26	I
Ru(bpy) ₃ ¹⁺ /0	-1.49	-1.45	-1.45	I
Ru(bpy) ₃ ⁰ /1 ⁻	-1.73	-1.69	-1.69	I

^aFormal potential, V vs. SCE in CH₃CN/0.1 M [n-Bu₄N]ClO₄.

^bPotential, V vs. SCE, of anodic peak in a cyclic voltammogram at a scan rate of 100 mV/sec using a Pt (smooth) working electrode in CH₃CN/0.1 M [n-Bu₄N]ClO₄.

^cPotential, V vs. SCE, of photoanodic peak in a cyclic voltammogram at a scan rate of 100 mV/sec using illuminated (632.8 nm) n-CdSe working electrode in CH₃CN/0.1 M [n-Bu₄N]ClO₄. These are typical data for freshly etched electrode surfaces using the Br₂/CH₃OH etch.

^dClass I, II, III, IV, and V behavior is given in the text.

Table II. Auger Data for n-CdSe Electrodes After Various Pretreatments

Surface Pretreatment ^a	Cd/Se Ratio ^b
conc. HCl	5 ± 1
Br ₂ /CH ₃ OH	1 ± 0.5
Na ₂ S ₂ O ₄ /NaOH	6 ± 1
HNO ₃ /H ₂ SO ₄ /HOAc/HCl	1 ± 0.5
K ₂ Cr ₂ O ₇ /HNO ₃	1 ± 0.5
Ar ⁺ Sputtered	7.5 ± 0.5

^aEtches used and Ar⁺ sputtering conditions are described in the Experimental.

^bRatio of the peak-to-peak heights of the Cd (376 eV) and Se (1315 eV) Auger signals, uncorrected for elemental sensitivity.

Table III. Comparison of Barrier Heights at n-CdSe/Metal or Liquid Electrolyte Interfaces

Metal (ϕ , V) ^a	Barrier Height, E_g , eV ^b	Redox Couple (E° , V vs. SCE) ^c	Barrier Height, E_g , eV ^c \pm 0.1 V
Pt (5.30)	0.37	TMPD ^{2+/1+} (0.7)	0.6
Au (4.75)	0.49	(biferrocene) ^{2+/1+} (0.5)	0.76
Cu (4.53)	0.33	Fe(η^5 -C ₅ H ₅) ₂ ^{1+/0} (0.43)	0.77
Ag (4.40)	0.43	(biferrocene) ^{1+/0} (0.28)	0.88
		TMPD ^{1+/0} (0.10)	0.56
		Fe(η^5 -C ₅ Me ₅) ₂ ^{1+/0} (-0.12)	0.80
		MY ^{2+/1+} (-0.45)	0.35
		MY ^{1+/0} (-0.85)	0.26
		Ru(bpy) ₃ ^{2+/1+} (-1.3)	"Ohmic"
		Ru(bpy) ₃ ^{1+/0} (-1.49)	"Ohmic"
		Ru(bpy) ₃ ^{0/-1} (-1.73)	"Ohmic"

^aData for work functions of metals are from Ref. 10a.

^bData for n-CdSe/metal barrier heights are from Ref. 6.

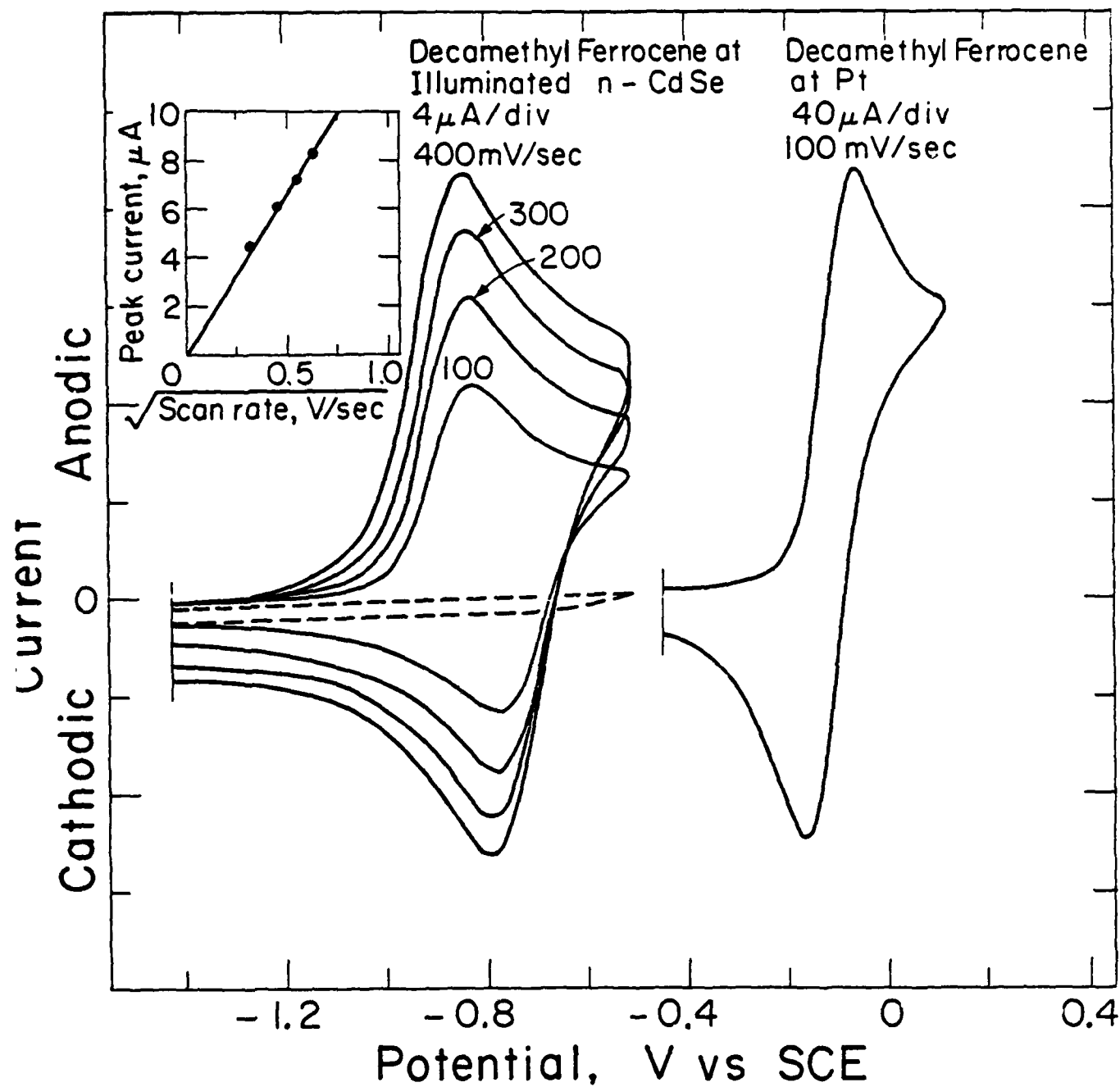
^cThis work. Barrier height, E_g , is taken as the difference in photoanodic current peak at CdSe and at Pt, Table I, in the cyclic voltammogram at 100 mV/sec scan rate. "Ohmic" refers to a situation where E_g is 0.0 and essentially reversible electrochemistry is observed. These data are ± 0.10 eV and are culled from a variety of measurements of the sort represented in Figures 1 and 2 and Table I.

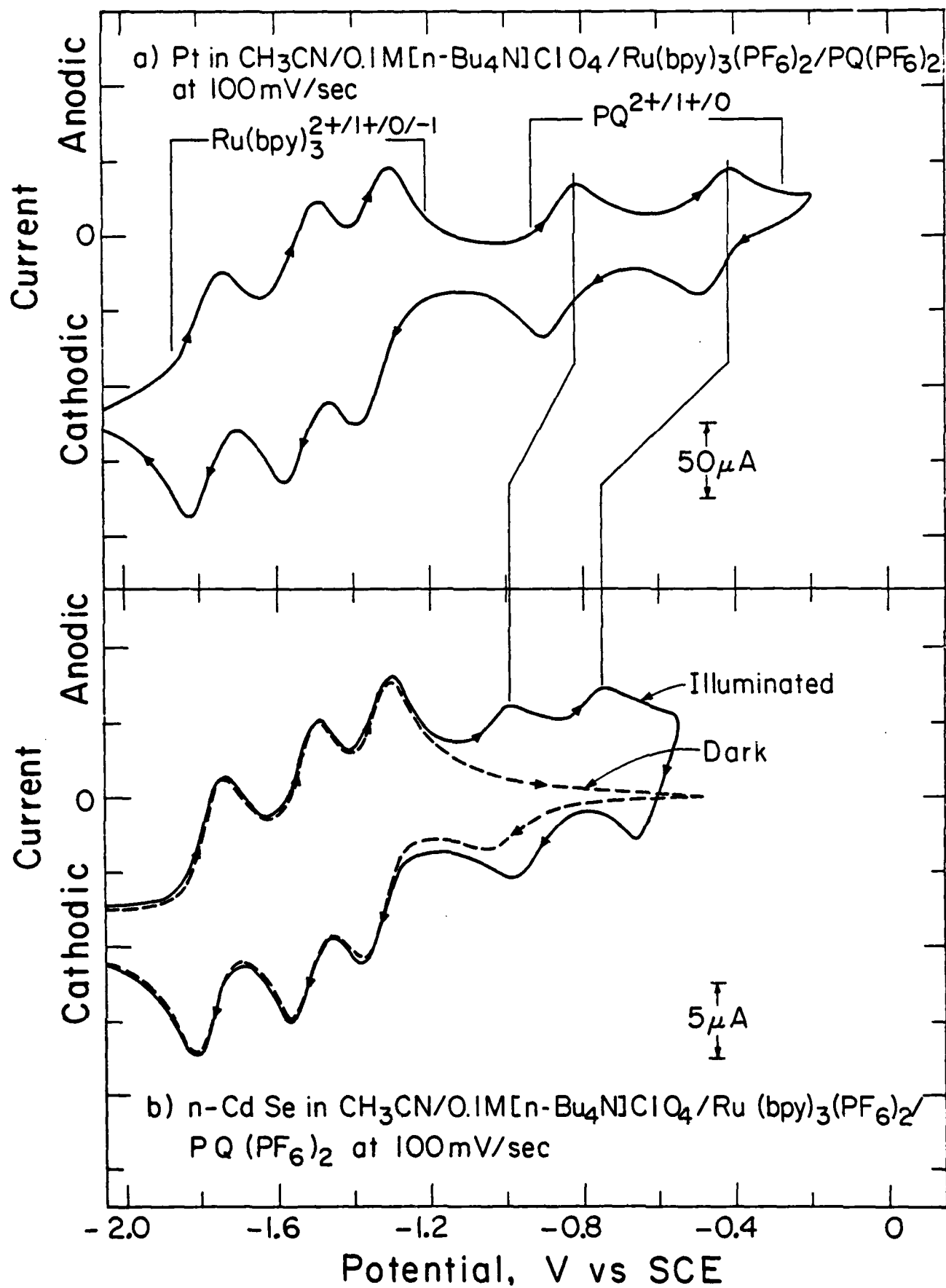
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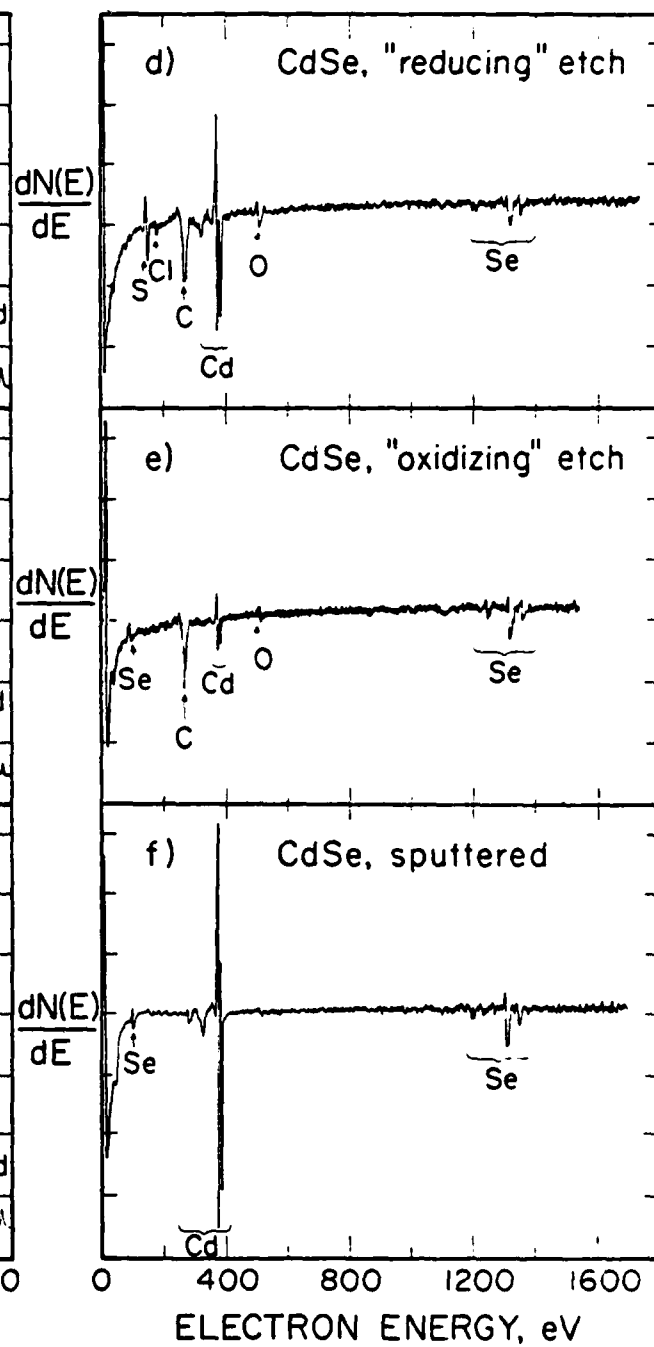
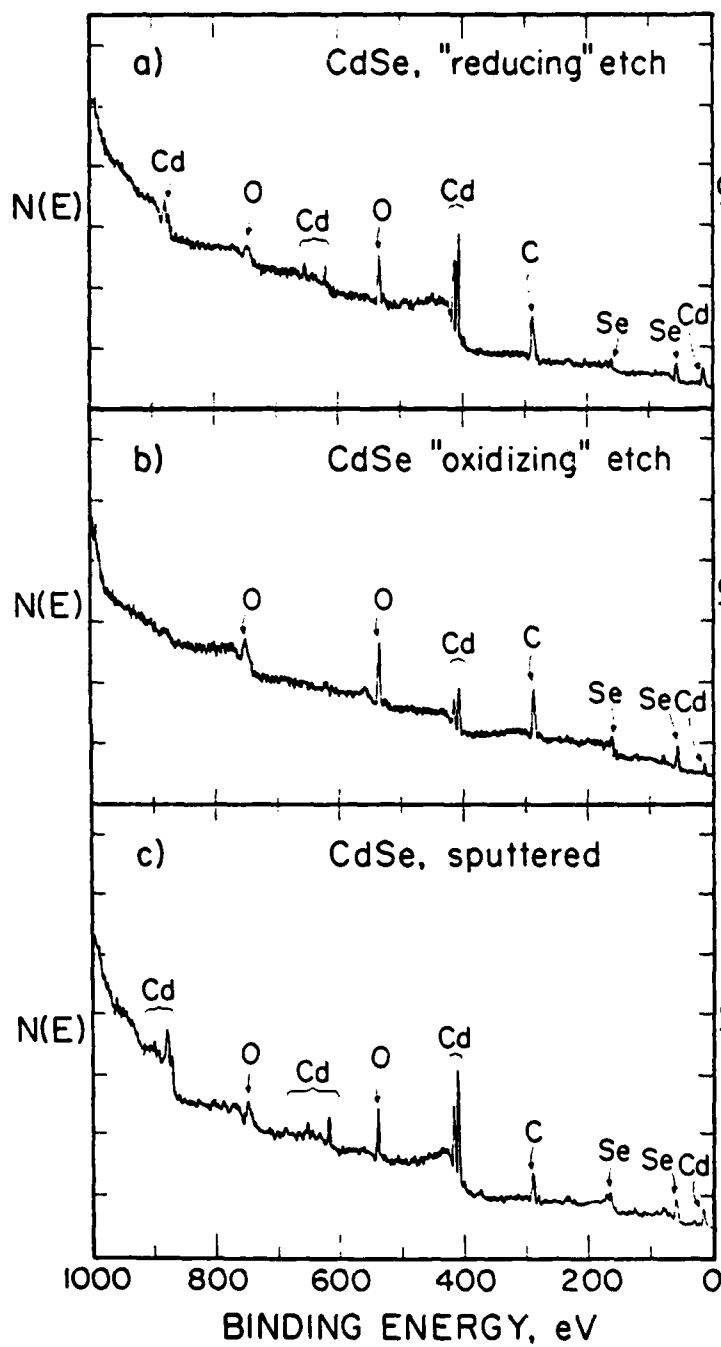
Figure 1. Cyclic voltammetry for $\sim 1 \text{ mM Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ at illuminated n-CdSe (pretreated with Br_2/MeOH etch) in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ and at Pt. Different current scales are due to different electrode areas. The dashed curve is for n-CdSe in the dark. Inset shows the scan rate dependence for the photoanodic current peak at n-CdSe. In all cases the initial potential is the negative potential limit.

Figure 2. Comparison of cyclic voltammetry at Pt (a) and at illuminated (—), 632.8 nm, $\sim 50 \text{ mW/cm}^2$) and dark (-----) n-CdSe (b) in the presence of $\sim 1 \text{ mM N,N'}$ -dimethyl-4,4-bipyridinium, PQ^{2+} , and $\sim 1 \text{ mM Ru}(\text{bpy})_3^{2+}$ in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$. For these scans the initial potential is -2.2 V vs. SCE ; consequently, the scan in the dark shows nearly no reducible PQ^{2+} , since no PQ^{2+} is made in the dark positive sweep owing to the position of E_{FB} .

Figure 3. Comparison of XPS (left) and Auger spectra (right) for n-CdSe pretreated with a reducing etch ($\text{NaOH}/\text{Na}_2\text{S}_2\text{O}_4$), an oxidizing acid etch ($\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HOAc}/\text{HCl}$), and sputtered with Ar^+ in the spectrometer until no changes in relative signals occurred.







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